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Single Vibronic Level Fluorescence. II. Vapor-Phase Fluorescence Spectra from the Zero-Point Level of ${}^1B_{2u}$ Benzene and Benzene- d_6 *

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Fluorescence spectra have been obtained at 300°K from C_6H_6 and from C_6D_6 vapor at 0.1 torr in which all emitting molecules are in the zero-point vibrational level of the ${}^1B_{2u}$ state. Analysis of the spectra are completed using selection rules appropriate for D_{6h} symmetry of both the ground (${}^1A_{1g}$) and excited (${}^1B_{2u}$) states. The spectra are compared with the zero-point fluorescence obtained by the conventional method of matrix isolation of benzene at 77°K. The forbidden transitions seen in the latter are absent in isolated molecule gas-phase spectra. The zero-point spectra are also compared with that from a 300°K Boltzmann distribution of ${}^1B_{2u}$ vibronic levels.

INTRODUCTION

In the first paper of this series,¹ we described the general appearance of vapor-phase fluorescence spectra that originated from some single vibronic levels (SVL fluorescence) of the first excited singlet (${}^1B_{2u}$) state of benzene. In the present report we will describe in detail one of those SVL fluorescence spectra. We will discuss fluorescence originating from the zero-point or "vibrationless" level of the ${}^1B_{2u}$ state of C_6H_6 and of C_6D_6 .

This fluorescence is obtained by pumping ground-state molecules directly into the upper-state zero-point level with gas pressures sufficiently low to preclude any collisional change of vibrational energy before radiative decay. Pumping of the zero-point level is achieved by use of "monochromatic" light tuned to the 6_1^0 absorption band² of benzene. Gas pressures on the order of 0.1 torr or less are low enough to allow fluorescence decay prior to collisional perturbations.⁵

Previous techniques of obtaining fluorescence from the zero-point level in benzene have centered on use of exciting light that populates higher vibrational levels in the excited singlet state combined with some method of removing vibrational energy in excess of zero point before fluorescence occurs. In the vapor phase this has been approximated by simply using high pressures of gas so that fluorescence occurs from a 300°K Boltzmann distribution of vibrational states.⁶ Unfortunately, the spectrum resulting from that procedure contains its predominant contributions from the vibrational levels above the zero-point level.

In condensed phase, use of a solid matrix containing benzene at low temperature has been more successful in producing a zero-point level fluorescence spectrum.⁷ However, the matrix spectrum cannot be expected to be equivalent to that of an isolated molecule due to interactions of benzene with its host. This is clearly evident in the fluorescence spectra from benzene in solids where site splittings can be observed. In fact, even the formally forbidden 0, 0 band appears in these spectra. A question which must be resolved concerns how much, if any, of such structure is intrinsic to the isolated fluorescing molecule and how much is induced by the environment. A comparison of these low-tem-

perature spectra with the SVL fluorescence described in the present report should help answer this question.

EXPERIMENTAL

Many of the details of the experimental techniques have been described previously.¹ The principle problem attendant with obtaining a spectrum from the zero-point level of the ${}^1B_{2u}$ state centers about low fluorescence intensity. This is a result of having to use a weak exciting source which is centered on a weak absorption band in a very low-pressure gas. In addition, the fluorescence is dispersed to obtain a spectrum, and this means that no more than about 1% of the fluorescence wavelength region can be examined at one time.

A Hanovia 500-W Xenon compact arc coupled with a $\frac{3}{4}$ -m Czerny-Turner spectrometer (Spex Industries, Model 1700) is used as the source of "monochromatic" radiation tunable to the 6_1^0 absorption band of C_6H_6 and of C_6D_6 . The maximum of this band is at 37 482 cm^{-1} (vac) in C_6H_6 and at 37 712 cm^{-1} in C_6D_6 .³ The spectrometer, used in the third order with a 1200-lines-per-mm grating, supplies a bandpass of about 50 cm^{-1} when operated with 1-mm slitwidths. This bandwidth is sufficiently narrow to limit observable excitation to the 6_1^0 band. We estimate the beam power of this "monochromatic" exciting light to be on the order of 10^{-7} W.

The 6_1^0 absorption band used to reach the zero-point level of the ${}^1B_{2u}$ state is weak because absorption occurs only from ground-state molecules with one quantum of $\nu_6'' = 608$ cm^{-1} thermally excited.⁸ The Boltzmann factor for this vibration is 0.054 at 300°K, and as a result the "effective pressure" of benzene molecules accessible to us for pumping to the upper state is reduced to only about 5% of the actual pressure. In order to excite a sufficient number of molecules to yield observable fluorescence, multipass optics are used. A fluorescence cell in the shape of a cross was made from 3- and 4-in.-i.d. Pyrex tubing. The cell is shown in Fig. 1. The mirror configuration across the shorter dimension is after the design of White⁹ as modified by Herzberg,¹⁰ and it provides a 2.0-m absorption path for the pumping light. This path is folded about the geometric center of the fluorescence capture

optics contained in the longer arms. With this absorption path, about 15% of the exciting beam is absorbed by 0.1 torr of benzene. The longer cell arms contain a set of spherical mirrors after the design of Welsh¹¹ as described in our previous paper.¹ Quartz optics following the design of Callomon¹² image the fluorescence from this cell into a $\frac{3}{4}$ -m scanning Czerny–Turner spectrometer. The use of an exciting beam crossed with the fluorescence capture optics reduced scattered excited light in the fluorescence spectrum to negligible intensity (see Figs. 3 and 4). The intensity of scattered exciting light is now three orders of magnitude less than that obtained with a different fluorescence cell described in the first paper of this series.¹ The fluorescence intensity obtained with the two cells is comparable.

A cooled EMI 6256SA photomultiplier is used for fluorescence detection. Both photon counting and direct current amplification of the photomultiplier output were tried, and the former was found to give a superior signal-to-noise ratio. All the spectra reported here use photon counting, in which a Hewlett–Packard 5201L scaler–timer is set to count the number of photons detected by the photomultiplier in consecutive 12-sec intervals. This count is converted to an analog signal and displayed on a strip chart recorder as the fluorescence spectrometer slowly scans over wavelength to give conventional plots of fluorescence intensity vs wavelength. The tallest bands in Fig. 3 correspond to 75 photon/sec and the weakest to approximately 1 photon/sec detected by the photomultiplier. The average dark current of the photomultiplier is 1.5 event/sec and comprises the total background. The noise in the spectrum is attributable almost entirely to statistical fluctuations in the stochastic signal rather than to lamp fluctuations.

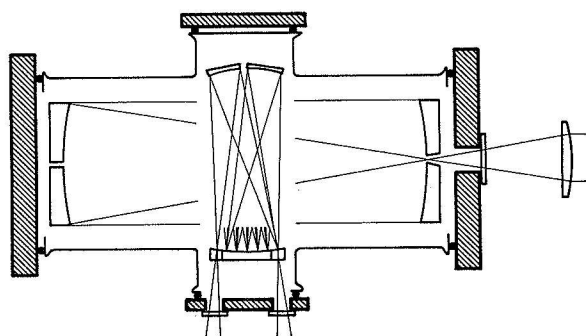


FIG. 1. Gas-phase fluorescence cell (not to scale). The end plates are aluminum, and a greaseless vacuum seal to the Pyrex cell is obtained with neoprene O-rings. The mirrors are mounted on the end plates and are externally adjustable with glass and Teflon feedthroughs [C. S. Parmenter and M. W. Schuyler, *Rev. Sci. Instr.* **39**, 611 (1968)]. The mirrors have a reflectivity of 0.9 between 2500 and 3500 Å. The distance between the mirrors creating the folded absorption path is 12.5 cm. The Welsh mirrors for fluorescence capture are located 45 cm apart and have an effective aperture of $f/5$. These mirrors provide a theoretical fluorescence capture enhancement of approximately a factor of 10 relative to a cell without mirrors. Fluorescence is imaged through the gap between the front pair of Welsh mirrors.

TABLE I. The location of band maxima in C_6H_6 fluorescence (from Fig. 3).

Displacement (cm^{-1}) ^a		
Observed	Calculated	Assignment
0	0	$6_1^0 1_0^0$
993	993	$6_1^0 1_1^0$
1988	1986	$6_1^0 1_2^0$
2982	2979	$6_1^0 1_3^0$
3979	3972	$6_1^0 1_4^0$
170	189	$16_2^0 1_0^0$
1176	1182	$16_2^0 1_1^0$
2185	2175	$16_2^0 1_2^0$
3178	3168	$16_2^0 1_3^0$
1322	1326	$17_2^0 1_0^0$
2320	2319	$17_2^0 1_1^0$
3318	3312	$17_2^0 1_2^0$
4301	4305	$17_2^0 1_3^0$
467	465	$11_1^0 16_1^0 1_0^0$
1454	1458	$11_1^0 16_1^0 1_1^0$
2444	2451, 2488	$11_1^0 16_1^0 1_2^0, 7_1^0 1_0^0$ ^b
3451	3444, 3481	$11_1^0 16_1^0 1_3^0, 7_1^0 1_1^0$
4429	4437, 4474	$11_1^0 16_1^0 1_4^0, 7_1^0 1_2^0$
571	570	$9_1^0 1_0^0$
1573	1563	$9_1^0 1_1^0$
2549	2556	$9_1^0 1_2^0$
3550	3549	$9_1^0 1_3^0$
4560	4542	$9_1^0 1_4^0$
797	798	$6_1^0 16_2^0 1_0^0$
1783	1791	$6_1^0 16_2^0 1_1^0$
2787	2784	$6_1^0 16_2^0 1_2^0$
3779	3777	$6_1^0 16_2^0 1_3^0$
1701	1692	$6_1^0 10_2^0 1_0^0$
2683	2685	$6_1^0 10_2^0 1_1^0$
3664	3678	$6_1^0 10_2^0 1_2^0$
4677	4671	$6_1^0 10_2^0 1_3^0$
...	1084	$10_2^0 1_0^0$
2078	2077	$10_2^0 1_1^0$
3069	3070	$10_2^0 1_2^0$
4070	4063	$10_2^0 1_3^0$

^a The displacements are to lower energy from the 6_1^0 origin at 37 478 cm^{-1} . The column of calculated displacements uses frequencies given in Table III.

^b These pairs of transitions occur too close together to be resolved in Fig. 3.

A conventional vacuum line containing no mercury or grease is used for gas handling. It is maintained at 10^{-6} torr between runs. Benzene pressures are established by expansion from small volumes using an all-metal Bourdon gauge. The C_6H_6 and C_6D_6 samples¹³ are degassed before use and stored in glass vessels.

RESULTS

Population of the Zero-Point Level

The relationship between the 6_1^0 absorption band in C_6H_6 and the intensity profile of the exciting light used

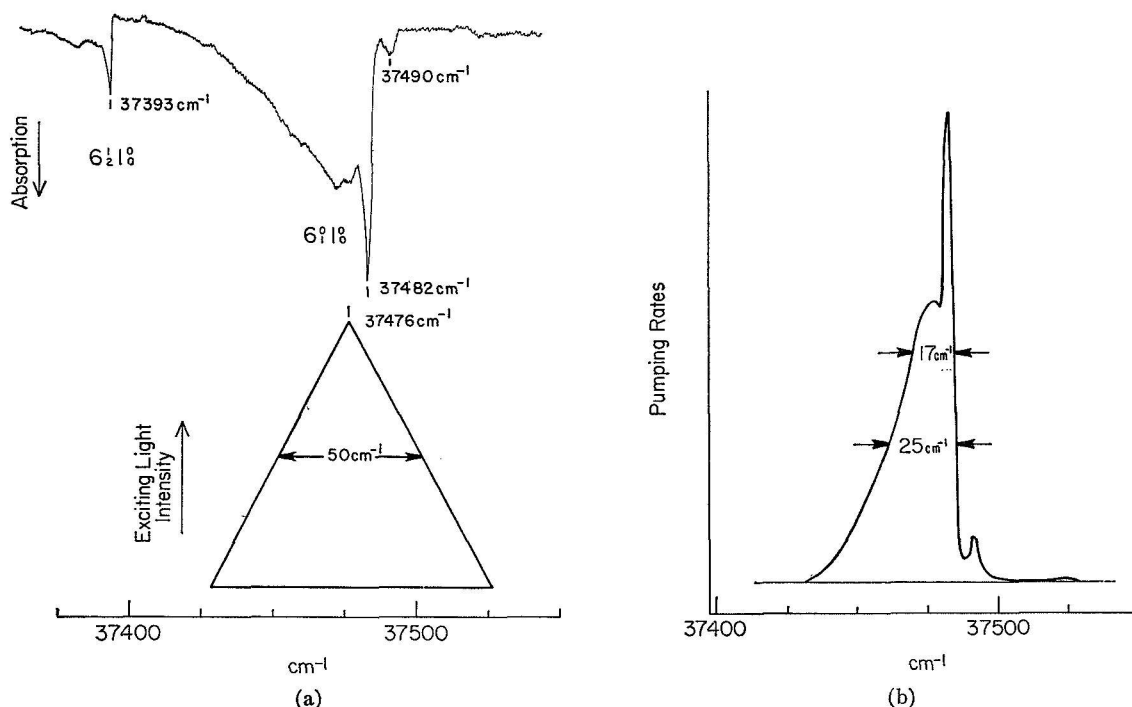


FIG. 2. (a) the profiles of excitation and absorption in C_6H_6 for these fluorescence experiments. The upper trace is the absorption spectrum in the region of interest at 1.5-cm^{-1} resolution. The principal maximum at $37\,482\text{ cm}^{-1}$ in that spectrum is that of the 6_1^0 band. The intensity of that band falls to zero within a few wavenumbers at higher energy but a long rotational tail (with a subsidiary maximum near $37\,475\text{ cm}^{-1}$) of this vibrational transition is observed at lower energies.⁸ The small band at $37\,393\text{ cm}^{-1}$ (assignment 6_2^1) does not absorb the exciting light significantly. The band at $37\,490\text{ cm}^{-1}$ lying on the shoulder of the 6_1^0 band is unassigned and may account for as much as 3% or 4% of the absorption. (b) The product of spectral contours of the exciting light and absorption band shown in Fig. 2(a). This product approximates the relative pumping rates in absorption, and it can be seen that the resulting profile is narrower than either the absorption or excitation spectra distributions.

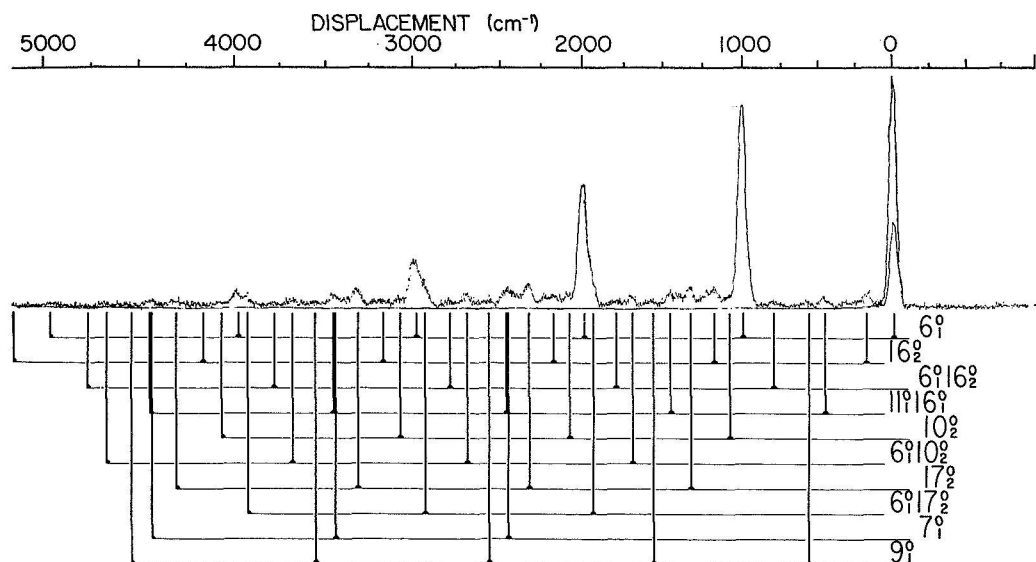


FIG. 3. The spectrum of fluorescence from the zero-point energy level of the ${}^1B_{2u}$ state of benzene- h_6 vapor. The scattered exciting light appears under the prominent fluorescence band at 0-cm^{-1} displacement, and it is the only feature in the otherwise flat background underlying the spectrum. The band at 0-cm^{-1} displacement has its maximum at $37\,476\text{ cm}^{-1}$. There is no detectable fluorescence to higher energies. The bandpass of the fluorescence spectrometer is 48 cm^{-1} .

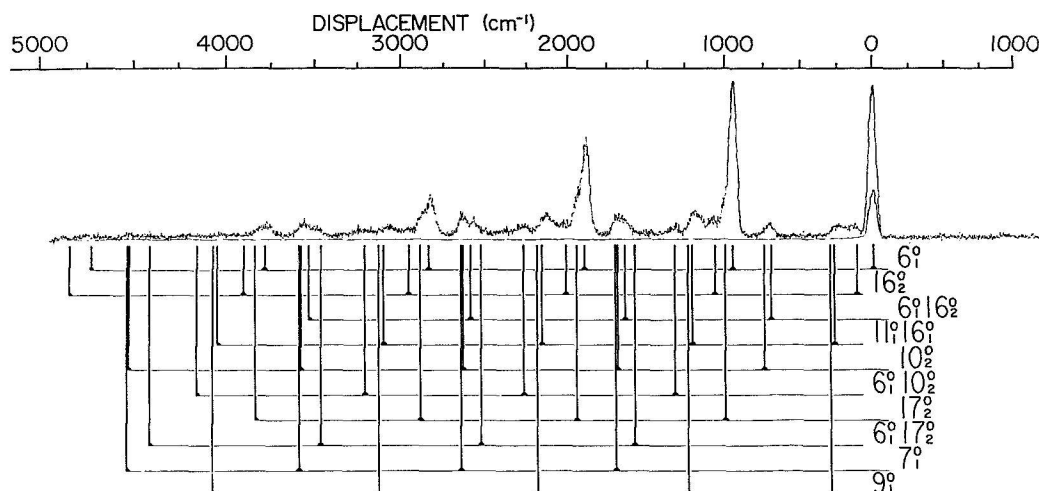


FIG. 4. The spectrum of fluorescence from the zero-point energy level of the ${}^1B_{2u}$ state of benzene- d_6 vapor. The band at 0-cm $^{-1}$ displacement has its maximum at 37 703 cm $^{-1}$. The other comments for Fig. 3 apply also to this spectrum.

for this work is shown in Fig. 2(a). The intensity profile of the exciting light is determined principally by the slit function of the monochromator. The product of this profile and the absorption band gives an indication of the energy spread in the excited states produced by

TABLE II. The location of band maxima in C_6D_6 fluorescence (from Fig. 4).

Displacement (cm $^{-1}$) ^a		
Observed	Calculated	Assignment
0	0	$6_1^0 1_0^0$
943	946	$6_1^0 1_1^0$
1882	1891	$6_1^0 1_2^0$
2827	2837	$6_1^0 1_3^0$
3764	3782	$6_1^0 1_4^0$
127	115	$16_2^0 1_0^0$
1078	1061	$16_2^0 1_1^0$
2021	2007	$16_2^0 1_2^0$
2958	2953	$16_2^0 1_3^0$
235	263, 289	$11_1^0 16_1^0 1_0^0, 9_1^0 1_0^{0b}$
1191	1209, 1235	$11_1^0 16_1^0 1_1^0, 9_1^0 1_1^0$
2127	2155, 2181	$11_1^0 16_1^0 1_2^0, 9_1^0 1_2^0$
3065	3101, 3127	$11_1^0 16_1^0 1_3^0, 9_1^0 1_3^0$
4033	4046, 4072	$11_1^0 16_1^0 1_4^0, 9_1^0 1_4^0$
704	695, 740	$6_1^0 16_2^0 1_0^0, 10_2^0 1_0^0$
1687	1640, 1686, 1694	$6_1^0 16_2^0 1_1^0, 10_2^0 1_1^0, 7_1^0 1_0^0$
2566, 2639	2586, 2632, 2640	$6_1^0 16_2^0 1_2^0, 10_2^0 1_2^0, 7_1^0 1_1^0$
3563	3532, 3578, 3586	$6_1^0 16_2^0 1_3^0, 10_2^0 1_3^0, 7_1^0 1_2^0$
(4524)	4478, 4524, 4532	$6_1^0 16_2^0 1_4^0, 10_2^0 1_4^0, 7_1^0 1_3^0$
1314	1320	$6_1^0 10_2^0 1_0^0$
2270	2266	$6_1^0 10_2^0 1_1^0$
(3242)	3211	$6_1^0 10_2^0 1_2^0$

^a The displacements are to lower energy from the 6_1^0 origin at 37 709 cm $^{-1}$. The column of calculated displacements makes use of the frequencies given in Table III. The displacements in parentheses indicate very broad, weak bands with uncertain maxima.

^b These sets of bands lie too close together for resolution in Fig. 4.

absorption of the pumping light. This is shown in Fig. 2(b). It is apparent that the pumping light is effectively limited to the 6_1^0 band, and furthermore, it covers the entire band. As a result, a complete Boltzmann spread of rotational states will be produced in the excited electronic state, but their relative populations will be distorted from that of a normal distribution because of the nonuniform intensity of the exciting light across the absorption band. This distorted population will be reflected in fluorescence. Fluorescence bandwidths will be approximately equal to the excitation profile shown in Fig. 2(b). Half-height bandwidths are expected to be about 30 cm $^{-1}$, and this is observed in Figs. 3 and 4.

Fluorescence Spectra

The SVL fluorescence spectrum from the zero-point level of the ${}^1B_{2u}$ state of C_6H_6 is shown in Fig. 3, and that for C_6D_6 is displayed in Fig. 4. Both spectra are linear in wavelength so that their wavenumber scale is compressed to short wavelengths. The spectral response of the detection apparatus is almost constant throughout the spectral region of fluorescence, and the actual relative band intensities are approximately as shown. (The fluorescence detection sensitivity drops by only about 15% at the low wavenumber end relative to the region of the exciting light. This attenuation is caused principally by the decreasing grating efficiency in the fluorescence spectrometer.)

The positions of the fluorescence bands are listed as displacements from the exciting line in Tables I and II. Location of the maxima of the weaker bands in these spectra is somewhat arbitrary, and these displacements must in general have an uncertainty of about 10 cm $^{-1}$.

DISCUSSION

The assignment of the SVL fluorescence spectra from the ${}^1B_{2u}$ zero-point level in C_6H_6 and C_6D_6 is based on the previously established selection rules for the ${}^1B_{2u}$ -

TABLE III. Ground-state frequencies of vibrational modes that are active in the gas-phase ${}^1B_{2u}$ - ${}^1A_{1g}$ spectrum of C_6H_6 and C_6D_6 .

Symmetry	Coordinate ^a	Fundamentals ^b (cm^{-1})	
		C_6H_6	C_6D_6
a_{1g}	1 (2)	993	946
a_{1g}	2 (1) ^c	3073	2303
e_g	6 (18)	608	580
e_{2g}	7 (15)	3056	2274
e_{2g}	8 (16) ^c	1596	1558
e_{2g}	9 (17)	1178	869
e_{1g}	10 (11)	846	660
a_{2u}	11 (4)	674	496
e_{2u}	16 (20)	399	347
e_{2u}	17 (19)	967	787

Allowed binary combinations: $(e_{1g})^2$, $(e_{2g})^2$, $(e_{2u})^2$, $e_{2g} \times a_{2g}$, $e_{2u} \times a_{2u}$, $e_{1g} \times e_{1g}$, $e_{2g} \times e_{2g}$, $e_{2u} \times e_{2u}$.

^a We have used the numbering of Wilson (Ref. 2). The numbers in parentheses are those of G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, Princeton, N. J., 1945).

^b We have used frequencies selected by Callomon, Dunn, and Mills³ except for that of ν_1 (C_6H_6). A value of 993 is a more accurate choice for this fundamental.

^c These modes are included in our table to complete the symmetry group, but they are not active in our spectra.

${}^1A_{1g}$ transition in benzene vapor.¹⁴ No deviations from these rules are required to explain our spectra, and no irregularities with respect to other gas-phase fluorescence or absorption assignments in benzene have been found. The spectra are completely consistent with D_{6h} symmetry of the ${}^1B_{2u}$ state in the gas phase. The features found in condensed-phase fluorescence indicating departure from excited-state D_{6h} symmetry are absent in our fluorescence spectra.

General Criteria Used for Assignments

If isolated benzene molecules in the vapor phase have D_{6h} symmetry in both the ${}^1B_{2u}$ and the ${}^1A_{1g}$ states, optical transitions between the two must be vibronically induced.¹⁴ Since fluorescence originates from the vibrationally symmetric zero-point level of the excited state, vibrational levels reached in the ground state must contain an e_{2g} component. For example, the excited state can in principle combine with the ground state in which a fundamental of any of the four e_{2g} modes is excited. Alternately, the fluorescence transition can leave excited in the ground state a combination of vibrations that possesses an e_{2g} component. Some possible binary combinations are listed by symmetry groups in Table III.

In addition to the selection rules established by symmetry considerations, it is an empirical observation based on analysis of the gas-phase absorption spectrum

and on the fluorescence spectra from other vibronic levels^{1,15} that only certain vibrations in benzene have significant activity in the ${}^1B_{2u}$ - ${}^1A_{1g}$ transition. The principal vibrational features of both absorption and fluorescence can be assigned with the assumption that 5 of the 10 vibrational symmetry groups in benzene are predominantly active. The present spectrum appears to be consistent with this observation. The vibrations contained in the active symmetry groups are listed with their ground-state frequencies for C_6H_6 and C_6D_6 in Table III. Eight of those 10 vibrations are used in our assignments.

Two additional aspects of the SVL fluorescence spectra in Figs. 3 and 4 are important. First, these spectra are very much like the Stokes part of a Raman experiment in that they consist of a series of bands occurring only at wavelengths longer than that of the exciting line. These transitions are simply equivalent to the 0, 0 band energy ($38\,086\,cm^{-1}$)³ minus vibrational energy left excited in the ground state. Those vibrational levels in the ground state left excited by fluorescence are subject to the symmetry restrictions cited above, and a glance at Table III shows that the maximum energy available for a fluorescence transition from the zero-point level is that of the 6_1^0 transition. This lies at $38\,086 - 608 = 37\,478\,cm^{-1}$ in the case of C_6H_6 and is coincident with the exciting line. Thus, all other fluorescence transitions are found at lower energies. The fluorescence spectrum will therefore

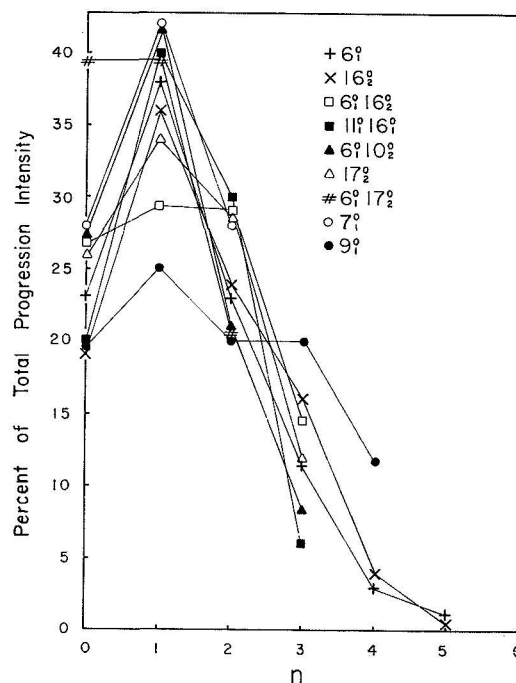


FIG. 5. Franck-Condon factors in the fluorescence from the zero-point level of ${}^1B_{2u}$ benzene. This is a plot of the relative intensities in Fig. 3 of the progression members 1_n^0 from a variety of origins, where $n=0, 1, \dots$. The total intensity contained in each progression has been normalized so that the comparison of the intensity envelopes is more easily seen.

consist of a series of bands that begins at a wavelength coincident with the exciting light and that continues to longer wavelengths as successively higher vibrational levels in the ground electronic state are left excited. The spectrum is expected to be discrete at least in transitions near the exciting line since these must involve low-lying discrete vibrational levels in the ground state.

A second feature of these spectra (and also of the absorption spectra) is the prominence of progressions in the totally symmetric ring breathing mode, ν_1 . In emission from the zero-point level of the first excited singlet state, the progression built on the origin 6_1^0 would be $6_1^0 1_0^0$, $6_1^0 1_1^0$, $6_1^0 1_2^0$, and so forth. The ν_1 progression is also built on other origins. As a result, the analysis of the fluorescence spectrum can be summarized as an ensemble of ν_1 progressions built upon those various origins 6_1^0 , 16_2^0 , 7_1^0 , etc., that are consistent with the symmetry restrictions cited above and which involve vibrational modes listed in Table III.

Intensities in the ν_1'' Progressions

Figure 5 gives a comparison of the relative intensities of members of the ν_1'' progression formed on a number of different origins in the C_6H_6 spectrum. Since the relative intensities are set by the overlap integral $\langle \nu_1' = 0 | \nu_1'' = n \rangle$, they should be nearly identical for every progression. This is approximately true, at least to the extent that we are able to make quantitative measurements on weak bands. In every case, maximum intensity occurs in the $\nu_1' = 0 \rightarrow \nu_1'' = 1$ band. We have used these progression intensity relationships as an additional criterion in assignment, rejecting alternate assignments in which relative intensity ratios show significant deviation from the patterns in Fig. 5.

Assignment of C_6H_6 Zero-Point Fluorescence

The specific assignments of the spectra in Fig. 3 are indicated in the schematic under the spectrum and in Table I. More detailed comments concerning these assignments follow. It can be noted in these comments that vibronic combinations in fluorescence always correspond to analogous combinations observed in absorption. This is apparent in fluorescence from every vibronic level we have examined,¹ and it provides yet another criterion to use in making fluorescence assignments.

The Origin 6_1^0

The most intense bands of the spectrum are members of the progression $6_1^0 1_n^0$ with $n = 0, 1, 2, \dots$. The first member, 6_1^0 , is coincident with the exciting line position. These bands correlate with the most intense bands in the absorption spectrum, the so-called A bands,¹⁶ which form the progression $6_1^0 1_n^0$. A small contribution to the intensity of the $6_1^0 1_n^0$ fluorescence bands may also come from the origin 16_4^0 which has a displacement

of 986 cm^{-1} from the exciting line, as well as from the origin $11_1^0 17_1^0$ at 1033-cm^{-1} displacement. All of these weak bands would be too close to the intense $6_1^0 1_n^0$ bands for resolution in our experiments. The origin 16_0^4 and also the combination of ν_{11} and ν_{17} can be assigned in absorption.¹⁵

The Origin 16_2^0

The analogous origins 16_2^0 and 16_0^2 are present in the absorption spectrum of benzene vapor.³ Some additional intensity in the $16_2^0 1_n^0$ fluorescence bands may arise from another transition if collisions cause any upward vibrational relaxation to the first level above the zero level in the excited state. This first level is ν_{16}' , and it lies only 237 cm^{-1} above the zero-point level. A very strong transition, $6_1^0 16_1^1$, will occur from that level with a displacement of 162 cm^{-1} from the exciting light. The band in Fig. 3 (a spectrum taken at about 0.1 torr pressure) is seen at a displacement of $175\text{--}180 \text{ cm}^{-1}$, close to the 189-cm^{-1} displacement calculated for the 16_2^0 transition. However, as benzene pressure is increased to the range 0.5–1 torr, the band center moves to a 160-cm^{-1} displacement. This most reasonably is ascribed to the $6_1^0 16_1^1$ transition which becomes predominant as collisions populate the ν_{16}' level.

The Origin 17_2^0

We find a progression with displacements 1322, 2320, 3316, and 4301 cm^{-1} and have assigned it $17_2^0 1_n^0$ (calculated origin 1326 cm^{-1}). In Paper I¹ we had assigned a similar progression in other spectra to $6_1^0 11_2^0$ (calculated $1348, 2341 \text{ cm}^{-1} \dots$), but due to the consistent 25-cm^{-1} error in predicted position, this has now been rejected in favor of the 17_2^0 assignment. 17_2^0 is found in the absorption spectrum.¹⁵ Again, an alternate possibility occurs if there is significant collisional relaxation upward to the $2\nu_{16}' = 474\text{-cm}^{-1}$ vibronic level prior to fluorescence. The transition $6_1^0 16_2^2$ could then occur at 323, 1315, $2309 \text{ cm}^{-1} \dots$ with strong intensity. However, this seems an unlikely assignment to use for Fig. 3. First, we are unable to observe reproducibly in spectra at 0.1 torr the band at 323-cm^{-1} displacement that must also occur if the $6_1^0 16_2^2 1_1^0$ transition contributes measurably to the band observed at 1322 cm^{-1} . (The 323-cm^{-1} band can be seen to grow in when gas pressure is raised above 0.5 torr.) Second, if the level $2\nu_{16}'$ were sufficiently populated to be observed at 0.1 torr, the $6_1^0 16_1^1$ band from the level ν_{16}' should also be observable, and as discussed above, it is not. Finally, the intensity ratios (Fig. 5) of the bands in this progression are consistent with a progression origin at 1320 cm^{-1} rather than at 320 cm^{-1} .

The Origins $11_1^0 16_1^0$ and 7_1^0

Origins analogous to both of these fluorescence origins are observed in the absorption spectrum³ with

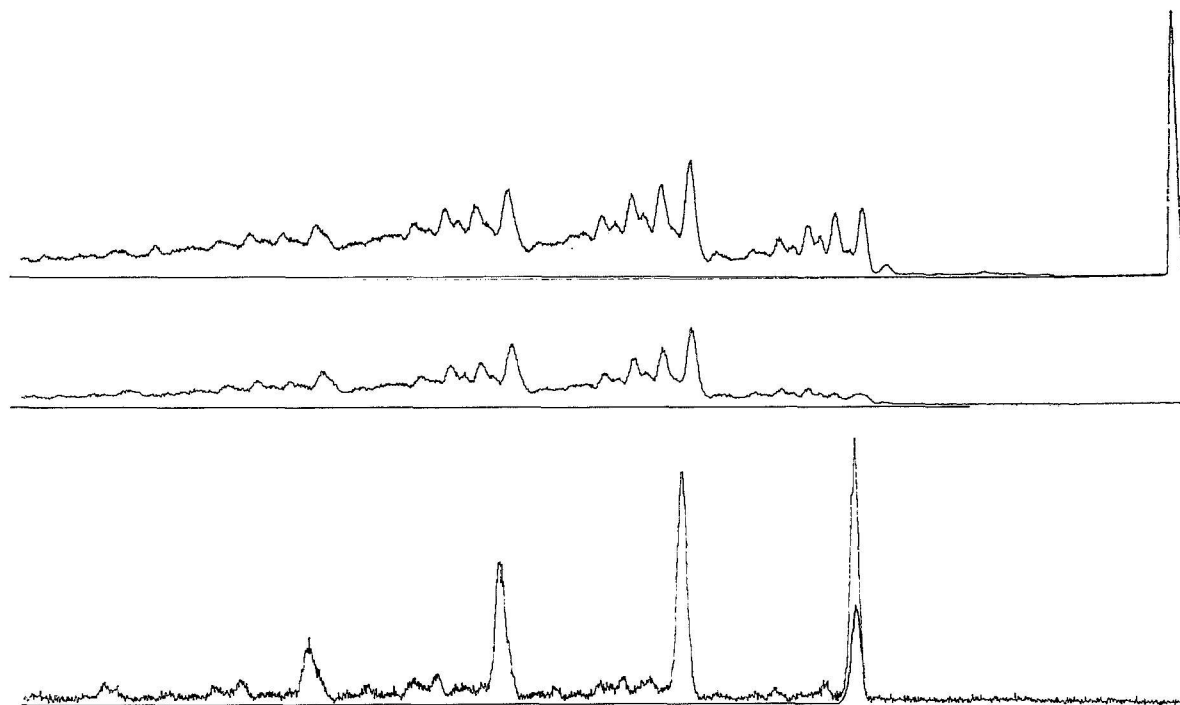


FIG. 6. A comparison of the spectrum of fluorescence from the zero-point level with those from a 300°K Boltzmann distribution of vibrational levels in the ${}^1B_{2u}$ state of benzene- h_6 vapor. The bottom spectrum, taken from Fig. 3, is from the zero-point vibrational level. The upper spectra are each from a Boltzmann distribution of vibrational levels obtained by addition of isopentane at a heat bath. The top spectrum is from 0.1 torr of C_6H_6 in the presence of 100 torr of isopentane using the 2537-Å Hg line to excite the upper state of benzene. The intense band at the far right is Rayleigh scattered 2537-Å radiation. The features in the spectrum have been assigned by F. M. Garforth and C. K. Ingold, *J. Chem. Soc.* **1948**, 427. The center spectrum is obtained from 8 torr of benzene with 92 torr of added isopentane and is excited with radiation identical to that used for the bottom spectrum. The center spectrum closely matches the top spectrum with the exception of the first group of bands on the right. Reabsorption of fluorescence by benzene at high pressure distorts these bands from their true intensities.

moderate intensities. For example, progressions based on $11_0{}^116_0^1$, $11_1{}^016_0^0$, $11_1{}^016_0^1$, and $11_0{}^116_1^0$ all occur in absorption. In fluorescence from the zero-point level, the displacements due to progression members on the origins $11_1{}^016_0^0$ and 7_1^0 would lie too close together (22 cm^{-1}) to be resolved with our present apparatus. We can, however, obtain an indication of the relative intensities of each progression by use of the expected Franck-Condon factors. The first two bands in the progression (465 and 1454 cm^{-1}) concern the transitions $11_1{}^016_1{}^01_0^0$ and $11_1{}^016_1{}^01_1^0$ only. From these two band intensities, we can predict with Fig. 5 the intensities in the remaining members of the progression $11_1{}^016_1{}^01_n^0$ with $n \geq 2$. We then subtract these estimated intensities from the bands at 2444 , 3451 , and 4429 cm^{-1} which contain also intensity from the transitions 7_1^0 , $7_1^01_1^0$, and $7_1^01_2^0$, respectively. The residue represents the intensities of the progression built on 7_1^0 , and as can be seen in Fig. 5, those intensities form a Franck-Condon envelope that is qualitatively correct.

The Origin 9_1^0

The progression beginning at a displacement of 570 cm^{-1} from the exciting line correlates well with the predicted position of the 9_1^0 origin. The origin 9_0^1 is

active in the absorption spectrum,¹⁵ and we therefore expect to see it in fluorescence. Some additional intensity may be contributed to the second and succeeding members of this progression by a nearly coincident progression based on $6_1^016_4^0$. However, its contribution to $9_1^01_n^0$ intensities must be small since it is shown in Fig. 5 that relative intensities of the bands in the progression starting at 570-cm^{-1} displacement are about correct for a single origin.

The Origin $6_1^010_2^0$

Both $6_0^110_0^2$ and $6_1^010_0^2$ are seen in absorption, again with moderate intensity. A possible alternate fluorescence progression built on $6_1^04_1^05_1^0$ could occur 6 cm^{-1} to the red of the $6_1^010_2^0$ bands, but we are unable to find evidence for significant activity of these modes in absorption, and they probably do not contribute measurable intensity to our spectrum.

The Origin $6_1^017_2^0$

A shoulder appears on the third and higher members of the strong fluorescence progression $6_1^01_n^0$ (see Fig. 3). This is consistent with the predicted appearance of the origin $6_1^017_2^0$. The analogous transitions are seen in

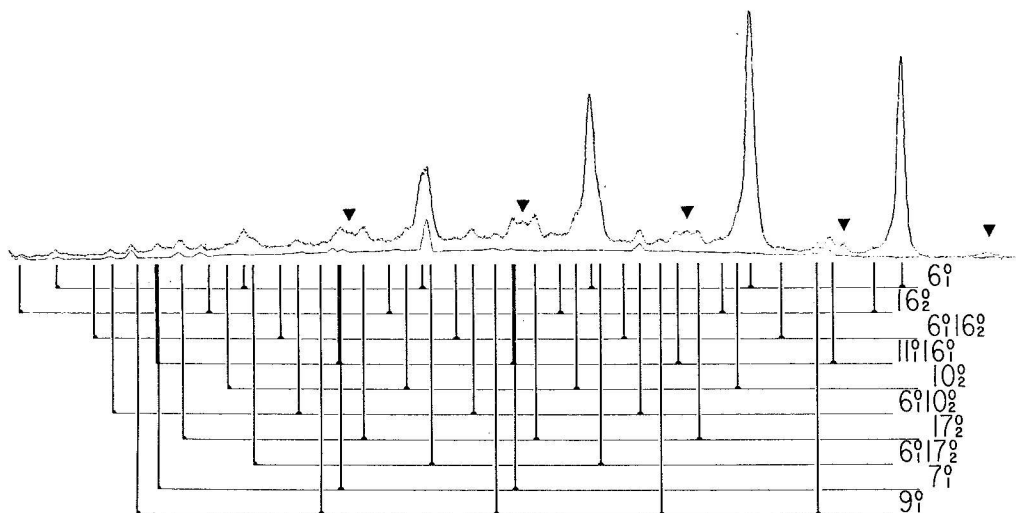


FIG. 7. The spectrum of fluorescence from $10^{-3} M$ benzene- h_6 in solid cyclohexane at 77°K. The spectral resolution of this spectrum has been set to match that of Fig. 3. The assignment scale has been taken directly from Fig. 3 to facilitate comparison. The triangular indicies mark a progression not present in the vapor phase spectrum of Fig. 3. The origin of that progression is about 600 cm^{-1} to higher energy from the 6_1^0 band common to both spectra.

absorption. It is difficult to measure the intensity ratios for this progression due to the proximity of the strong $6_1^0 1_n^0$ bands, but the ratios are qualitatively acceptable.

The Origin 10_2^0

There are three bands at 2078, 3069, and 4070 cm^{-1} which are assigned to the second, third, and fourth members of the progression $10_2^0 1_n^0$. The progression origin should occur at 1084 cm^{-1} and may account for the weak bump at the base of the strong $6_1^0 1_1^0$ band. The intensities of these progression members are too uncertain to measure accurately and are not shown in Fig. 5. They appear to be qualitatively correct. 10_0^0 has been assigned in absorption.³

Assignment of C_6D_6 Zero-Point Fluorescence

The close correspondence of the assignment of C_6D_6 fluorescence with those of C_6H_6 fluorescence is evident from Figs. 3 and 4. The same set of vibronic origins describes each spectrum, and we shall not discuss them in detail for C_6D_6 . As in C_6H_6 fluorescence, the strongest bands in the C_6D_6 spectrum are members of the ν_1'' progression formed on the origin 6_1^0 . Some origins seen in the C_6H_6 spectrum are partly obscured in C_6D_6 because they overlap members of other progressions. The origins $6_1^0 16_2^0$ and 10_2^0 , for example, are nearly coincident, and the origin 7_1^0 in turn becomes coincident with the second members of those overlapping progressions. The origins $11_1^0 16_1^0$ and 9_1^0 also lie too close together for separate resolution in our spectra. In addition, use of the previously reported frequencies of these vibrations does not predict accurately the position of the maxima in the progression assigned to them (see Table II). The ground-state frequencies of ν_{11} and ν_{16} are well established,¹⁷ but these frequencies predict a band position on the order of 30 cm^{-1} from

that observed. We believe that the presence of another origin, 9_1^0 , is responsible for the shifted maximum. The frequency of ν_9'' has been previously assigned as about 869 cm^{-1} .^{3,18} However, no band maxima appear in Fig. 4 at the positions predicted in this value. The vibration is prominent in the fluorescence from benzene- h_6 , and on the basis of the correspondence of activity of all other active modes in C_6H_6 and C_6D_6 , we expect it to be prominent in benzene- d_6 as well. For this reason, we propose that the transition 9_1^0 is active in the C_6D_6 spectrum, and that the frequency of ν_9'' is close to 810 cm^{-1} . This adjustment yields a satisfactory prediction of the broad band resulting from the two close origins 9_1^0 and $11_1^0 16_1^0$. However, we cannot be conclusive about this revision; and its validity must await further confirmation.

Comparison with Higher-Pressure Fluorescence

In the introduction, we described two methods that have previously been used to approximate fluorescence from the zero-point level. Both used a heat bath to remove excess vibrational energy from the $^1B_{2u}$ electronic state before fluorescence occurs. The use of high gas pressure¹⁹ as the heat bath establishes at 300°K a Boltzmann vibrational distribution that can be shown by simple calculation to contain only a minor fraction of its population in the zero-point level. This is a result of the numerous low-frequency modes in benzene. This fact is also evident when the emission spectra from excitation into zero-point levels at low and at high pressures are compared. Such a comparison is given in Fig. 6. Examination of the spectra in that figure shows that the high-pressure spectrum consists of emission that is predominantly from levels other than the zero-point level. We estimate that only about 18% of the intensity in the high-pressure spectrum is con-

tained in bands originating from the zero-point level.²¹ In fact, we can see transitions in the high-pressure spectrum that originate from a vibrational level 1234 cm^{-1} above the zero-point energy. Obviously, a 300°K heat bath cannot be used to approximate excitation to the zero-point level or to study the electronic decay from the zero-point level as has on occasion been claimed in the past.

Comparison with Low-Temperature Benzene Fluorescence

Numerous reports have been published concerning the fluorescence of benzene in a 77°K heat bath consisting of a solid-phase solvent.⁷ This heat bath also establishes a Boltzmann equilibrium of vibrational levels in the ${}^1B_{2u}$ state before fluorescence occurs, and analysis of the spectra shows that the emission origin is effectively limited to the zero-point level. Those spectra should therefore compare closely with our gas-phase spectra except for features that may be introduced by site interactions between benzene and its solid-phase host.

In Fig. 7 we display a fluorescence spectrum from benzene in a cyclohexane matrix at 77°K. This spectrum is compared with the gas-phase spectrum of Fig. 3 by simply underlaying it with the assignments used for Fig. 3. The good correlation of gas-phase assignments with the solid spectrum is evident. The principal difference between the two lies in an extra progression in the solid spectrum whose origin is about 600 cm^{-1} to higher energy than the transition 6_1^0 . This origin is the electronic 0, 0 band commonly observed in condensed-phase benzene fluorescence. The progression formed on the 0, 0 band is a prominent feature of the condensed-phase spectrum, and it is comparable in intensity with any of the other structure except the very intense progression built on the origin 6_1^0 .

We have made a careful search for corresponding totally symmetric and hence forbidden transitions in the gas phase. By reducing the scattered light relative to our first SVL fluorescence experiments (compare Fig. 3 with the corresponding spectrum in Paper I) we are able to examine areas near the exciting line where these symmetric transitions are expected to occur. In the gas-phase spectrum, the 0, 0 band would lie 608 cm^{-1} to higher energies from the exciting line, and the more intense 1_1^0 transition would lie 384 cm^{-1} to the red of our exciting line. No transitions are detectable in Fig. 3 at those frequencies. It is apparent that the forbidden features in the ${}^1B_{2u} \rightarrow {}^1A_{1g}$ fluorescence transition in condensed-phase benzene are induced predominantly (or probably entirely) by site interaction of benzene with its host.

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† Lubrizol Fellow 1969–1970; NASA Trainee 1966–1969.

¹ C. S. Parmenter and M. W. Schuyler, *J. Chim. Phys.* (to be published). We refer to this as Paper I on SVL fluorescence.

² We use the notation of Callomon, Dunn, and Mills.³ A vibronic band in the ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition is given as X_n^m where n represents the quanta of vibrational mode X in the lower state and m the quanta in the excited state. For example, a band designated as $6_1^0 1_2^0$ represents the transition between the zero-point level of the excited state and the ground state in which one quantum of ν_6'' and two quanta of ν_{12}'' are excited. We use the normal mode numbering of Wilson,⁴ since this appears in most of the papers concerned with the electronic spectroscopy of benzene.

³ J. H. Callomon, T. M. Dunn, and I. M. Mills, *Phil. Trans. Roy. Soc. London Ser. A* **259**, 499 (1966).

⁴ E. B. Wilson, Jr., *J. Chem. Phys.* **3**, 276 (1934).

⁵ We cannot claim that collisional effects are entirely absent at these pressures, but they are sufficiently small so that emission from levels other than that populated in absorption is not important at the resolution of our fluorescence spectra. At high resolution, the effect of collisions on higher vibrational levels in benzene can be clearly observed at 0.1 torr. See C. S. Parmenter and A. H. White, *J. Chem. Phys.* **50**, 1631 (1969).

⁶ G. B. Kistiakowsky and M. Nelles, *Phys. Rev.* **41**, 595 (1932); G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.* **4**, 9 (1936); C. K. Ingold and C. L. Wilson, *J. Chem. Soc.* **1936**, 941; F. M. Garforth and C. K. Ingold, *ibid.* **1948**, 427.

⁷ J. D. Spangler and H. Sponer, *Spectrochim. Acta* **19**, 169 (1963) and references therein; S. Leach, R. Lopez-Delgado, and L. Grajar, *J. Chim. Phys.* **63**, 194 (1966) and references therein; J. D. Spangler and N. G. Kilmer, *J. Chem. Phys.* **48**, 698 (1968) and references therein.

⁸ The 0, 0 band is forbidden in benzene and absent from the gas-phase absorption spectrum. The 6_1^0 band is the most intense band that can be used to reach the zero-point level of the ${}^1B_{2u}$ state.

⁹ J. U. White *et al.*, *J. Opt. Soc. Am.* **32**, 285 (1942); **41**, 732 (1951); **45**, 154 (1955).

¹⁰ H. J. Bernstein and G. Herzberg, *J. Chem. Phys.* **16**, 30 (1948).

¹¹ H. L. Welsh *et al.*, *J. Opt. Soc. Am.* **41**, 712 (1951); **45**, 338 (1955).

¹² J. H. Callomon, *Can. J. Phys.* **34**, 1046 (1956).

¹³ The C_6H_6 is fluorometric grade obtained from Matheson, Coleman and Bell. The C_6D_6 was obtained from Merck, Sharp & Dohme.

¹⁴ A nice summary of the benzene selection rules is given by T. M. Dunn, in *Studies on Chemical Structure and Reactivity*, edited by J. H. Ridd (Methuen, London, 1966), p. 103.

¹⁵ G. H. Atkinson, C. S. Parmenter, and M. W. Schuyler (unpublished results).

¹⁶ F. M. Garforth and C. K. Ingold, *J. Chem. Soc.* **1948**, 417.

¹⁷ ν_{11} is well established because of its prominence in the infrared spectrum of perdeuterobenzene, and ν_{16} is known accurately because it forms sequences in the electronic absorption spectrum.

¹⁸ G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, Princeton, N.J., 1945), p. 364.

¹⁹ Studies by M. Stockburger *et al.*,²⁰ and by L. M. Logan, I. Buduls, and I. G. Ross, in *Molecular Luminescence*, edited by E. C. Lim (Benjamin, New York, 1969) have shown that on the order of 100 torr of an efficient quencher is required to bring the ${}^1B_{2u}$ state into nearly complete vibrational equilibration before fluorescence occurs.

²⁰ H. Kemper and M. Stockburger, *Ber. Bunsenges. Physik. Chem.* **72**, 1044 (1968); M. Stockburger, *ibid.* **72**, 151 (1968); *Z. Phys. Chem. (Frankfurt)* **35**, 179 (1962).

²¹ We obtain this number by comparing the area under the entire high-pressure spectrum in Fig. 6 with the part due to the vibrationless level. The area due to the latter is obtained by normalizing the area due to the latter is obtained by normalizing the area of the vibrationless spectrum in Fig. 3 through use of the relative intensities of the $6_1^0 1_1^0$ bands in the two spectra.

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